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(54) **Deeply drawn can and method of producing the same.**

(57) A deeply drawn seamless can obtained by deeply drawing a steel plate having an organic coating which has corrosion resistance large enough to withstand highly corrosive acidic contents such as acidic beverages and sports beverages.

A tin-containing metal is applied onto the surface of the steel plate in a sea-island relationship maintaining a coating rate of 20 to 80% and, then, metal chromium and a hydrated chromium oxide are applied thereon in order to form an organic resin coating layer on the steel plate. The thus obtained can material is deeply drawn to form a can.

Background of the Invention

Field of the Invention:

5 The present invention relates to a seamless can obtained by deeply drawing a steel plate having an organic coating and to a method of producing the same. More particularly, the present invention relates to a deeply drawn corrosion-resistant can made of a laminated material of a metal substrate having a tin-containing metal that is coated at a rate that lies within a predetermined range and an organic coating layer, the can being suited for containing acidic beverages and sport beverages, and to a method of producing the same can.

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Prior Art:

Side-seamless can have heretofore been produced by subjecting a metal material such as an aluminum plate, a tin plate or a tin-free steel plate to the drawing of at least one stage between a drawing die and a punch to form a cup which consists of a drum portion with no seam on the side surface thereof and a bottom portion connected integrally to the drum portion without forming seam, and then, as required, squeezing the drum portion between a drawing punch and a squeezing die in order to reduce the thickness of the drum portion of the can. It has also been known to produce the side-seamless cans by using a material obtained by laminating a thermoplastic resin film such as a polypropylene of a thermoplastic polyester on the metal material.

20 Japanese Patent Publication Laid-Open No. 258822/1989 filed by the present inventors discloses a method of reducing the thickness of side walls of cans by effecting the bend-stretching at the time of the deep drawing, i.e., discloses a redrawing method wherein a predrawn cup of a coated metal plate is held by an annular holding member inserted in the cup and a redrawing die, a redrawing punch and the redrawing die are moved relative to each other in mesh with each other, the redrawing punch and the redrawing die being provided in concentric with the holding member and the redrawing die so as to be inserted in or come out from the holding member, thereby to form a deeply drawn cup having a diameter smaller than that of the predrawn cup, and wherein the radius curvature (RD) of the action corner of the redrawing die is 1 to 2.9 times as great as the thickness (tB) of the metal plate, the radius of curvature (RD) of the holding corner of the holding member is 4.1 to 12 times as great as the thickness (tB) of the metal plate, the plane engaging portions of the holding member and the redrawing die that engage with the predrawn cup have a dynamic coefficient of friction of 0.001 to 0.2, at least one stage of drawing is effected so that the redrawing ration defined as a ratio of the diameter of a shallowly drawn cup to the diameter of a deeply drawn cup lies over a range of 1.1 to 1.5, the whole side wall of the cup is uniformly bent in the direction of the height in order to reduce the thickness. It has also been proposed to use a tin-free steel (TFS: steel plate electrolytically treated with chromic acid) as a coated metal plate.

35 A material of cans consisting of TFS as a base material coated with an organic resin allows a resin coating layer to be intimately adhered thereto, and does not develop such a problem that the resin coating material is peeled off during the deep drawing or while the thickness is being as a result of drawing, during the neck-in treatment, double seaming relative to the cover, heat-sterilization treatment, or while the contents are being preserved. Therefore, the deeply drawn can made of such a material exhibit excellent processing properties.

40 In mass-producing the cans, however, defects and damages by the treatment may often develop in the organic resin coating material at a predetermined frequency permitting, sometimes, the underlying metal to be exposed. The coating on the TFS surface has a limited resistance against corrosion. Therefore, if the underlying metal is exposed, iron is abnormally eluted out or holes are formed resulting in the leakage when there are contained acidic beverages and spots beverages that cause the steel plate to be vigorously corroded.

45 In order to cope with the above problem, it can be contrived to treat the surface of the steel plate with tin or a tin alloy which exhibits corrosion-preventing effect that stems from the sacrificial dissolution of tin in order to impart corrosion-resistant property to the surface coating of the steel plate.

50 With the presently available tin-plated steel plates, however, intimacy or adhesiveness to the organic resin coating material is exhibited to a degree which is just enough to withstand a light degree of processing such as shallow drawing, but is not exhibited to a degree large enough to withstand the deep drawing and the subsequent neck-in processing and double lap-seaming.

Summary of the Invention

55 The object of the present invention therefore is to provide a deeply drawn can having excellent corrosion resistance which is capable of containing acidic beverages or sports beverages having large corrosion-promoting property and which can be deeply drawn or can be subjected to the treatment for reducing the thickness.

According to the present invention, there is provided a deeply drawn can having excellent corrosion resi-

stance made of a laminated material which comprises:

a metal substrate having a steel plate, a tin-containing metal applied thereon at a coating rate defined by the formula,

$$PSn = 100[1 - (VFe/VFeo)] \quad (1)$$

wherein VFe represents a photoelectric intensity of iron at a moment when the photoelectric intensity of iron (Fe) and the photoelectric intensity of tin (Sn) have entered into nearly a steady state while subjecting the surface of the steel plate to be coated an X-ray photoelectric spectroscopic method to etch the surface of said steel plate, and VFeo represents a photoelectric intensity of iron at a moment when the etching is further carried out and the photoelectric intensity of tin (Sn) becomes substantially zero,

of 20 to 80%, metal chromium and a hydrated chromium oxide which are applied onto the whole surface of the steel plate coated with the tin-containing metal; and

an organic resin coating applied onto the surface of said metal substrate.

In the material of cans used in the present invention, the tin-containing metal layer should be homogeneously and uniformly distributed on the steel plate substrate as a plated layer having a sea-island relationship with an average size in the plane direction of from 0.1 to 10 μm and, particularly, 0.2 to 5 μm . Further, the tin-containing metal layer should contain tin in an amount of greater than 20%, and should be in the form of a tin-plated layer, a tin-iron alloy layer, or a tin nickel-plated layer.

According to the present invention, furthermore, there is provided a redrawing method wherein the laminated member is drawn into a shallow predrawn cup, said predrawn cup is held by an annular holding member inserted in said cup and by a redrawing die, a redrawing punch and the redrawing die are moved relative to each other and in mesh with each other, said redrawing punch and said redrawing die being provided in concentric with said holding member and said redrawing die so as to move into and come out of the holding member, in order to form a deeply drawn cup having a diameter smaller than that of said predrawn cup, and the whole side wall of the cup is uniformly bent in the direction of the height to decrease the thickness of the side wall of the cup.

According to the method of the present invention, the radius of curvature (RD) of the action corner of the redrawing die is 1 to 2.9 times as great as the thickness (tB) of the metal plate, the radius of curvature (RD) of the holding corner of the holding member is 4.1 to 12 times as great as the thickness (tB) of the metal plate, the plane engaging portions of the holding member and the redrawing die that engage with the predrawn cup have a dynamic coefficient of friction of 0.001 to 0.2, and at least one stage of draw-molding is effected so that a redrawing ratio defined as a ratio of the diameter of the shallowly drawn cup to the diameter of the deeply drawn cup lies over a range of from 1.1 to 1.5.

A distinguished feature of the present invention is that the tin-containing metal is not applied as a completely continuous coating onto the steel plate substrate, but is applied in such a manner that the surfaces of the tin-containing metal and the steel surfaces exist being mixed together on the surface of the steel plate substrate, and that metal chromium and a surface-treated layer of a chromium oxide are formed on the above surface that is incompletely coated with the tin-containing metal. This makes it possible to greatly increase the corrosion resistance of the metal substrate itself as well as to greatly improve the adhesiveness between the metal substrate and the organic resin coating material to be capable of withstanding severe deep drawing and the reduction of thickness by bending and stretching the side walls.

Usually, the distribution of atoms on the metal substrate and the chemical composition can be measured by the X-ray photoelectric spectroscopic method. In the present invention, satisfactory results are obtained when the coating rate of the above-mentioned equation (1) lies from 20 to 80% and, preferably, from 30 to 60% as measured by the photoelectric spectroscopic method.

Fig. 1 shows the measure results of the metal substrate used in the present invention by the X-ray photoelectric spectroscopic method, wherein the abscissa represents the treatment time of when the steel plate is sputtered with argon ions. The sputtering for about 20 minutes corresponds to the etching quantity of about 300 angstroms. The ordinate represents the photoelectric intensities of the elements emitted by the irradiation with X-rays, i.e., represents the kinds and compositions of the metal exposed on the surface of the metal substrate. In the initial stage of etching as shown in Fig. 1, the electrons that are emitted are mostly those of chromium and chromium oxide, from which it is recognized that the outermost surface of the steel plate has been completely coated with chromium and chromium oxide. Then, as the etching proceeds, the emission of electrons from chromium and chromium oxide decreases, and the emission of electrons from tin and iron increase. That is, when the coating of the tin-containing metal is complete and is continuous, no electron is emitted from iron. However, the fact that the electrons are emitted from both tin and iron indicates that the iron-phase and the tin-phase exist being mixed together in the steel plate which is coated with the tin-containing metal but which is not coated with chromium yet. As the sputtering proceeds, the photoelectric intensity of tin and the photoelectric intensity of iron becomes nearly horizontal (steady state). In this case, it can be regarded

that the intensities are related to a ration of areas of the two metals on the reference surface (before being plated) of the steel plate. In the measurement of the present invention, the photoelectric intensity of iron at this moment is denoted by V_{Fe} . As the sputtering is further carried out, tin is removed by etching and the photoelectric intensity of tin becomes almost zero. At this moment, the surface of the steel plate consists almost all of iron. If the photoelectric intensity of iron at this moment is denoted by V_{Fe0} , then the ratio V_{Fe}/V_{Fe0} represents the ration of exposed areas of the steel plate. Therefore, a value obtained by subtracting the above ratio from 1 represents a coating factor of tin.

In the steel plate coated with the tin-containing metal used in the present invention, the steel plate assumes the sea-like distribution and the tin-containing metal layer assumes the island like-distribution. In additions, the tin-containing metal layer exists in a homogeneous and minute condition. Fig. 3 is a microphotograph of a tin plate having a coating rate PSn of a tin containing metal of 47% at a magnification of 400 times, wherein black portions are seas of the steel and white portions are islands of the tin-containing metal layer. The steel portions help increase the adhesive force of the organic resin coating layer via a metal chromium-chromium oxide layer, and the tin-containing metal layer portions elute out to prevent the underlying steel from corroding and to prevent the metal from eluting out. Therefore, even when the above can material is subjected to the deep drawing or to the treatment for reducing the thickness, the organic resin coating material does not at all peel off. Moreover, even when the organic resin coating material is partly damaged by the treatment, the damaged portions are not corroded by the acidic beverages or sports beverages.

Fig. 4 is a diagram of characteristic showing a change in the corrosion resistance (discoloration evaluation) when the coating rate PSn of the tin-containing metal is changed and a change in the adhesive force of the organic resin and chromium coating. It will be understood from Fig. 4 that the corrosion resistance suddenly increases as the coating rate PSn exceeds 20% and that the corrosion resistance decreases as the coating rate PSn exceeds 80% to make it difficult to perform the deep drawing. When the coating rate PSn is 100%, the adhesive force so decreases that the deep drawing can no longer be carried out even though the tin and metal chromium coatings are perfect (point P in Fig. 4).

Brief description of the Drawings

Fig. 1 is a graph showing the measured results of a surface-treated can material used in the present invention as measured by the X-ray photoelectric spectroscopic method;

Fig. 2 is a schematic diagram of the can material in cross section;

Fig. 3 is a microphotograph showing a particulate structure on the surface of the steel plate coated with the tin-containing metal that is used in the present invention;

Fig. 4 is a diagram showing correlations among the coating rate of tin on the can material, adhesive force of the organic coating material, and the corrosion resistance; and

Fig. 5 is a diagram of steps for drawing the can material.

Description of a Preferred Embodiment

A preferred embodiment of a deeply drawn can according to the present invention will now be described in conjunction with the accompanying drawings.

Fig. 2(A) is a schematic sectional view of the can material used in the present invention, wherein a surface-treatment layer 4 of a tin-containing metal is formed on the surface of a steel plate 2, and a surface-treatment layer 6 of metal chromium and a hydrated chromium oxide is further formed thereon. The layer 6 of metal chromium and hydrated chromium oxide is formed to completely cover the surface of the steel plate 2 and the surface of the tin-containing metal layer 4, and an organic resin layer 8 is further formed on the surface of the layer 6 of metal chromium and hydrated chromium oxide. The layer of chromium and hydrated chromium oxide and the organic resin layer 8 are drawn in Fig. 2(A) exaggerating the thickness. In the present invention, furthermore, the surface treatment layer 4 of the tin-containing metal is applied onto the surface of the steel plate 2 at a coating rate PSn over a range of from 20 to 80% as shown in Fig. 3.

Fig. 2(B) schematically illustrates the state in which the photoelectric intensities of tin and iron remain constant as measured by the X-ray photoelectric spectroscopic method mentioned earlier and wherein islands 9 of the tin-containing metal are floating on the sea of steel.

The steel plate substrate should generally be a rolled steel plate such as the one that has heretofore been used for producing cans. The steel plate should have a thickness of, usually, from 0.05 to 0.35 mm, and particularly from 0.07 to 0.30 mm though it varies depending upon the size of the final cans.

It is desired that the tin-containing metal is applied to the steel plate in an amount of 100 to 5000 mg/m^2 and, particularly, in an amount of 100 to 4000 mg/m^2 . When the coating amount becomes smaller than the

above range, the tin-containing metal layer 4 shown in Fig. 2(A) is not sufficiently formed, and the coating rate PSn may often become smaller than 20%. When the coating amount exceeds the above range, on the other hand, the coating rate PSn becomes too great and the adhesive force decreases.

The tin-containing metal may be an alloy with iron, nickel or any other metal, but its content should at least be greater than 20%. When the content of tin is smaller than the above-mentioned range, the corrosion resistance of the deeply drawn can is not sufficiently enhanced.

In order to form the tin-containing metal layer maintaining the sea-island relationship according to the present invention, the plated layer is precipitated in a granular form, and the plated steel plate is not subjected to the reflow processing but is washed with, for example, hydrochloric acid or a like acid of 1 to 7 N, so that the coating rate PSn lies within a range specified by the present invention.

In general, the coating rate PSn decreases with an increase in the degree of washing with acid. Therefore, the hydrochloric acid concentration, temperature of processing and the processing time should be suitably set on this basis.

Coating layer of metal chromium and hydrated chromium oxide.

The coating layer of chromium and a hydrated chromium oxide should be so provided as to sufficiently cover the surface of the steel plate and the surface of the tin-containing coating layer. A preferred example of the surface treatment is the electrolytic treatment with chromic acid to provide a metal chromium layer in an amount of 10 to 200 mg/m² and a chromium oxide layer in an amount of 1 to 50 mg/m² (reckoned as metal chromium). This layer is excellent in both organic film adhesion and corrosion resistance.

Organic resin coating layer.

Examples of the organic resin coating include a variety of thermoplastic resin films and thermosetting or thermoplastic resin films. Furthermore, preferred examples of the crystalline thermoplastic resin film include olefin-type resin films such as of polyethylene, polypropylene, ethylene-propylene copolymer, ethylene-vinyl acetate copolymer, ethylene-acrylic ester copolymer and ionomer; polyester films such as of polyethylene terephthalate, polybutylene terephthalate, ethylene terephthalate/isophthalate copolymer, ethylene terephthalate/adipate copolymer, ethylene terephthalate/sebacate copolymer, and butylene terephthalate/isophthalate copolymer; polyamide films such as nylon 6, nylon 6,6, nylon 11 and nylon 12; polyvinyl chloride films; and polyvinylidene chloride films. These films may be unstretched or may be biaxially stretched. Their thickness should generally be from 3 to 50 μm and, particularly, from 5 to 40 μm.

The film is laminated on the metal plate by the heat-melting method, the dry lamination or the extrusion coating method. When the adhesiveness (melt-adhering property) is poor, there can be interposed, for example, an urethane-type adhesive, an epoxy-type adhesive, an adhesive of the type of an acid-modified olefin resin, a copolyamide-type adhesive, a copolyester-type adhesive or an adhesive primer that is described below between the film and the metal plate. As the adhesive primer, there can be used a coating material that exhibits excellent adhesiveness to the metal plate, excellent anti-corrosion property, and excellent adhesiveness to the resin film. As the adhesive primer, there can be used an epoxy resin and a curing resin for the epoxy resin, such as a coating material consisting of a combination of a phenol resin, an amino resin, an acrylic resin and a vinyl resin, and particularly an epoxy-phenol coating material, or an organosol-type coating material composed of a vinyl chloride copolymer resin and an epoxy resin-type coating material. The adhesive primer or the adhesive agent should have a thickness of from 0.1 to 5 μm.

To effect the lamination, the adhesive primer or the adhesive agent is applied to either one or both of the metal and the film followed, as required, by drying or partial curing. Then, the two are pressed and adhered together into a unitary form under the application of heat. During the step of lamination, the biaxial molecular orientation in the film may slightly be loosened which, however, does not at all affect the drawing or the redrawing and may often turn out to be desirable from the standpoint of drawing operation.

Other compositions.

An inorganic filler (pigment) can be contained in the film for outer surface for the purpose of concealing the metal plate and assisting the transmission of wrinkle-suppressing force to the metal plate at the time of drawing and redrawing. Examples of the inorganic filler include inorganic white pigments such as rutile-type or anatase-type titanium dioxide, zinc flower, gloss white and the like; white body pigments such as barite, sedimenting barite sulfate, calcium carbonate, gypsum, sedimenting silica, aerosil, talc, sintered or unsintered clay, barium carbonate, alumina white, synthetic or natural mica, synthetic calcium silicate, and magnesium carbonate; black

pigments such as carbon black, magnetite, and the like; red pigments such as red iron oxide, yellow pigments such as sienna, and the like; and blue pigments such as ultramarine, cobalt blue, and the like. These inorganic fillers can be blended in an amount of 10 to 500% by weight and, particularly, in an amount of 10 to 300% by weight with respect to the resin.

5 A protective coating material that can be used instead of, or together with, the film may be any protective coating material comprising thermosetting and thermoplastic resins. Examples include modified epoxy coating materials such as phenol-epoxy coating material, amino-epoxy coating material; vinyl or modified vinyl coating materials such as vinyl chloride-vinyl acetate copolymer, partially saponified product of vinyl chloride-vinyl acetate copolymer, vinyl chloride-vinyl acetate-maleic anhydride copolymer, epoxy-modified, epoxyamino-modified, or epoxyphenol-modified vinyl coating material; acrylic resin-type coating material; and synthetic rubber-type coating material such as styrene-butadiene-type copolymer, and the like, which can be used alone or in a combination of two or more kinds.

10 These coating materials are applied to the metal material in the form of an inorganic solvent solution such as enamel, lacquer or the like, in the form of an aqueous dispersion or aqueous solution, or by the roller coating, spray coating, immersion coating, electrostatic coating, or electrophoretic coating. The above resin coating material is baked, as required as a matter of course, when it has a thermosetting property. From the standpoint of corrosion resistance and processability, it is desired that the protective coating material has a thickness (dry state) which is usually from 2 to 30 μm and, particularly, from 3 to 20 μm . In order to improve the drawing-redrawing property, furthermore, a variety of lubricating agents may be contained in the coated film.

20 Drawing.

In the steps of drawing and redrawing as shown in Fig. 5, a coated metal plate 10 is punched into a disc, a predrawn cup 13 having a bottom portion 11 and a side wall 12 is formed in a predrawing step using a predrawing punch of a large diameter and a die, the predrawn cup 13 is held by an annular holding member which is inserted in the cup and a redrawing die (not shown), a deeply drawn cup 16 having a diameter smaller than that of the predrawn cup is formed by moving a redrawing punch and the redrawing die in mesh with each other and relative to each other, the redrawing punch and the redrawing dies being provided in concentric with the holding member and the redrawing die so as to go into and come out from the holding member, and a cup 19 having a smaller diameter is formed by similarly effecting the drawing.

30 Reference numerals 14 and 17 denote bottom portions of the cups 16 and 19, and reference numerals 15 and 18 denote side walls of the cups 16 and 19. In carrying out the redrawing, it is desired to bend and stretch the coated metal plate by the action corner of the redrawing die in order to reduce the thickness, or to slightly squeeze the coated metal plate between the redrawing punch and the redrawing die during the redrawing steps in order to reduce the thickness.

In Fig. 5, the side walls of the cups usually have a relationship,

$$tw''' \leq tw'' \leq tw' \leq tB$$

It is desired that the drawing ratio defined by an equation,

$$\text{Drawing ratio} = (\text{diameter of material plate}) / (\text{Diameter of punch}) \quad (2)$$

40 usually lies within a range of from 1.2 to 2.0 and, particularly, from 1.3 to 1.9. It is further desired that the redrawing ratio defined by an equation,

$$\text{Redrawing ratio} = (\text{diameter of drawing punch}) / (\text{diameter of redrawing punch}) \quad (3)$$

usually lies within a range of from 1.1 to 1.6 and, particularly, from 1.15 to 1.5.

45 Furthermore, the degree of reduction of thickness of the side wall should usually be about 5 to 45 % and, particularly, about 5 to 40% of the thickness of the material plate (thickness of the bottom portion). It is desired that the drawing and redrawing are carried out under the conditions where molecular orientation takes place in the resin layer. For this purpose, the drawing and redrawing should be carried out at a stretching temperature of the resin layer, such as at a temperature of 20° to 200°C in the case of the PET.

In carrying out the drawing and redrawing, it is desired that the coated metal plate or the cup is further coated with various lubricants such as liquid paraffin, synthetic paraffin, edible oil, hydrogenated edible oil, palm oil, various natural waxes or polyethylene wax. The lubricant should be applied in an amount of usually from 0.1 to 10 mg/dm^2 and, particularly, in an amount of 0.2 to 5 mg/dm^2 though it may vary depending on the kind thereof. The lubricant is applied to the surface in a molten state by spray coating. The deeply drawn can that is obtained is then subjected to the after-treatment such as washing with water and drying, and is further subjected to the doming, trimming, neck-in treatment, bead treatment and flange treatment, in order to obtain a final barrel of can. Even in the above treatment steps, the organic resin coating material excellently follows the steel plate.

Examples and comparative Examples

Example 1:

5 A cold-rolled steel plate having a thickness of 0.15 mm and a tempering degree of DR-9 was washed with an acid and on which tin was plated using an ordinary stannous phenol sulphonate bath at a current density of 0.5 A/m² followed by washing with hydrochloric acid in order to obtain a tin-plated steel plate having a tin amount of 1.2 g/m² and a tin coating rate of 50%.

10 The tin-plated steel plate was then subjected to the ordinary electrolytic treatment with chromic acid to plate metal chromic in an amount of 120 mg/m² and to plate a hydrated chromium oxide in an amount of 15 mg/m² in a laminated form. The tin coating rate was calculated from the formula (1) by effecting the analysis based on the XPS (X-ray photoelectric spectroscopic) method.

15 A biaxially stretched polyethylene terephthalate film (melting point, 230°C) having a thickness of 20 μm to which has been applied an epoxyphenol-type adhesive primer was thermally adhered to a surface of the thus obtained steel plate that would become the inner surface of the can and, at the same time, a titanium dioxide-containing biaxially stretched polyethylene terephthalate/isophthalate film (melting point, 230°C) having a thickness of 15 μm to which has been applied a similar adhesive primer was thermally adhered to the surface of the steel plate that would become the outer surface of the can, in order to obtain a metal plate coated with resin. The palm oil was applied to the thus coated metal plate which was then punched into a disk having a diameter of 187 mm to form a shallowly drawn cup in accordance with the customary method. In the above drawing step, the drawing ratio was 1.4.

In the subsequent first, second and third redrawing steps, the cup was preheated at 80°C, and the redrawing was carried out. In the first to third redrawing steps, the redrawing conditions were as follows:

25	First redrawing ratio	1.25
	Second redrawing ratio	1.25
	Third redrawing ratio	1.25
30	Radius of curvature (Rd) of action corner of the redrawing die	0.40 mm

35 In order to reduce the thickness of the drum of can, the redrawing was effected by bending. The drawing and redrawing thus effected developed no problem in the processability, and the deeply drawn cup exhibited the following properties.

	Diameter of the cup	66 mm
	Height of the cup	140 mm
40	Rate of change in the thickness of side wall	-20%

Thereafter, the doming was effected according to a customary method, the palm oil was removed by washing with water and, then, the trimming was effected. Next, in the step of printing, printing was effected to the outer surface using an ordinary ink and a finishing varnish, followed by baking and neck-in/flange treatment, in order to obtain a deeply drawn coated can having a reduced thickness.

45 In this case, the rate of metal tin in the tin layer was 70% as measured by an electrochemical method (supplement to JIS-G3303) by using the bottom portion of the deeply drawn coated can as a sample and after the organic resin coating material was removed by being immersed in an aqueous solution of peroxide at 90°C.

50 The thus obtained deeply drawn coated can could be treated without permitting the coating material to be peeled off during the step of treatment. Thereafter, an orange juice was contained therein being heated at 95°C while permitting liquid nitrogen to drop thereon, and the cover was seamed. The orange juice was preserved for extended periods of time at 37°C to observe the corroding condition on the inner surface of the can pit corrosion and the leakage through the pore. No abnormal condition, however, was recognized. The results were as shown in Table 1.

55 Example 2:

A deeply drawn can was obtained by effecting the coating and treatment in the same manner as in Example 1 but plating tin in an amount of 3.2 g/m² and changing the tin coating rate into 76%. The results were as shown

in Table 1.

Example 3:

5 A deeply drawn can was obtained by effecting the coating and treatment in the same manner as in Example 1 but plating tin in an amount of 520 mg/m^2 and changing the tin coating rate into 26%. The results were as shown in Table 1.

Example 4:

10 A deeply drawn can was obtained by effecting the coating and treatment in the same manner as in Example 1 except that an alloy layer was formed on the interface between the tin layer and the steel and the ratio of metal tin in the tin layer was 45% since the biaxially stretched polyethylene terephthalate/isophthalate film was heat-adhered onto the plated steel plate at a temperature that was as high as nearly the melting point of the film. The results were as shown in Table 1.

Example 5:

20 A deeply drawn can was obtained by effecting the coating and treatment in the same manner as in Example 1 except that an epoxyphenol resin coating material was so applied and baked on the surface of the plated steel plate that would become the inner surface of the can that the thickness of the coated film after drying was $15 \mu\text{m}$ and the epoxyphenol resin coating material was so applied and baked on the surface that would become the outer surface of the can that the thickness of the coated film after drying was $15 \mu\text{m}$, the ratio of metal tin in the tin layer being 55%. The results were as shown in Table 1.

Comparative Example 1:

30 The coating and treatment were carried out in the same manner as in Example 1 except that the cold-rolled steel plate having a thickness of 0.15 mm and a tempering degree of DR-9 was washed with an acid on which tin was plated using an ordinary stannous phenol sulphonate bath at a current density of 1.5 A/m^2 to obtain a tin-plated steel plate having a tin amount of 3.7 g/m^2 and a tin coating rate of 100%, and then the tin-plated steel plate was subjected to the ordinary electrolytic treatment with chromic acid to plate metal chromium in an amount of 120 mg/m^2 and to plate a hydrated chromium oxide in an amount of 15 mg/m^2 in a laminated form. After the redrawing of the third time, however, the resin coating layer was partly peeled off on the drum portion of the cup, and the subsequent treatment could not be carried out.

Comparative Example 2:

40 A deeply drawn can was obtained by effecting the coating and treatment in the same manner as in Example 1 with the exception of using a so-called steel plate without tin that was obtained by washing the cold-rolled steel plate having a thickness of 0.15 mm and a tempering degree of DR-9 with an acid and subjecting the steel plate to an ordinary electrolytic treatment with chromic acid to plate metal chromium in an amount of 120 mg/m^2 and a hydrated chromium oxide in an amount of 15 mg/m^2 in a laminated form. The results were as shown in Table 1.

Comparative Example 3:

50 A deeply drawn can was obtained by effecting the coating and treatment in the same manner as in Example 1 except that tin was plated in an amount of 400 mg/m^2 and tin coating rate was 15%. The results were as shown in Table 1.

Comparative Example 4:

55 A deeply drawn coated can was obtained by effecting the coating and treatment in the same manner as in Example 1 except that it was plated in an amount of 3.8 g/m^2 and a tin coating rate was 85%. At the time of deep drawing, neck-in treatment and seaming, however, it was observed that the resin coating had been partly peeled off. The results obtained were as shown in Table 1.

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Table 1

	Tin coating rate (%)	Amount of metal tin (%)	Organic resin coating	Drawability	Neck-in workability	Seaming workability	Corrosion resistance (preserved at 37°C for 6 months)	Number of leaked cans N=100
Example 1	50	70	PET/PETI	○	○	○	○	(zero)
Example 2	76	78	same as above	○	○	○	○	(zero)
Example 3	26	58	same as above	○	○	○	○	(zero)
Example 4	60	45	same as above	○	○	○	○	(zero)
Example 5	80	56	epoxyphenol	○	○	○	○	(zero)
Comparative Example 1	100	80	PET/PETI	x	not evaluated			
Comparative Example 2	0	0	same as above	○	○	○	△ (some corroded points)	X (two cans)
Comparative Example 3	15	15	same as above	○	○	○	△ (some corroded points)	X (two cans)
Comparative Example 4	85	80	same as above	△	△	X (film floated partly)	X (many corroded points in film-floating portions)	○ (zero)

According to the present invention, a tin-containing metal is applied onto the surface of the steel plate at a coating rate of 20 to 80%, and then metal chromium and a hydrated chromium oxide are applied thereon, in order to form an organic resin coating layer on the steel plate which is then deeply drawn to obtain a can. Therefore, the organic resin coating layer of the deeply drawn can remains sufficiently adhered to the surface of the steel plate despite the presence of the tin-containing metal layer, and is not peeled off at all even after the aforementioned deep drawing, doming, trimming, neck-in treatment, beading and flange treatment. Moreover, since the tin-containing metal exists in an amount larger than a required amount, there takes place sacrificial dissolution of tin lending the cans well suited for storing even acidic beverages that have highly corrosive properties.

Claims

1. A deeply drawn can having excellent corrosion resistance made of a laminated material which comprises:
a metal substrate having a steel plate, a tin-containing metal applied thereon at a coating rate defined by the formula,

$$PSn = 100 \cdot 1 - (VFe/VFeo) \quad (1)$$

wherein VFe represents a photoelectric intensity of iron at a moment when the photoelectric intensity of iron (Fe) and the photoelectric intensity of tin (Sn) have entered into nearly a steady state while subjecting the surface of the steel plate to be coated to an X-ray photoelectric spectroscopy, at the etching treatment of the surface of said steel plate, and VFeo represents a photoelectric intensity of iron at a moment when the etching is further carried out and the photoelectric intensity of tin (Sn) becomes substantially zero,
of 20 to 80%, metal chromium and a hydrated chromium oxide which are applied onto the whole surface of the steel plate coated with the tin-containing metal; and
an organic resin coating applied onto the surface of said metal substrate.

2. A deeply drawn can according to claim 1, wherein the tin-containing metal layer consists of a tin layer, a tin-iron alloy layer, or a tin-nickel alloy layer.
3. A deeply drawn can according to claim 1, wherein the organic resin coating layer consists of a film layer of a biaxially stretched polyester or copolyester that is thermally adhered via an epoxy-phenol resin-type primer.
4. A deeply drawn can according to claim 1, wherein the metal chromium layer is provide in a coating amount of 10 to 200 mg/m² and the hydrated chromium oxide layer is provided in a coating amount of 1 to 50 mg/m² reckoned as a metal.
5. A deeply drawn can according to claim 1, wherein the tin-containing metal layer is homogeneously and uniformly distributed on the steel plate substrate as a plated layer having a sea-island relationship of an average size in the plane direction of 0.1 to 10 μm.

6. A redrawing method wherein a shallowly predrawn cup is formed by drawing a laminated material which comprises:
a metal substrate having a steel plate, a tin-containing metal applied thereon at a coating rate defined by the formula,

$$PSn = 100 \cdot 1 - (VFe/VFeo) \quad (1)$$

wherein VFe represents a photoelectric intensity of iron at a moment when the photoelectric intensity of iron (Fe) and the photoelectric intensity of tin (Sn) have entered into nearly a steady state while subjecting the surface of the steel plate to be coated to an X-ray photoelectric spectroscopy, at the etching treatment of the surface of said steel plate, and VFeo represents a photoelectric intensity of iron at a moment when the etching is further carried out and the photoelectric intensity of tin (Sn) becomes substantially zero,
of 20 to 80%, metal chromium and a hydrated chromium oxide which are applied onto the whole surface of the steel plate coated with the tin-containing metal; and
an organic resin coating applied onto the surface of said metal substrate;
and wherein said predrawn cup is held by an annular holding member inserted in said cup and by a redrawing die, a deeply drawn cup having a diameter smaller that of said predrawn cup is formed by

moving a redrawing punch and the redrawing die relative to each other in mesh with each other, said redrawing punch and said redrawing die being provided in concentric with the holding member and the redrawing die so as to go into and come out from the holding member, and the whole side wall of the cup is uniformly bent in the direction of the height to reduce the thickness of the side wall of the cup.

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7. A method according to claim 6, wherein the radius of curvature (RD) of the action corner of the redrawing dies is 1 to 2.9 times as great as the thickness (tB) of the metal plate, the radius of curvature (RD) of the holding corner of the holding member is 4.1 to 12 times as great as the thickness (tB) of said metal plate, the plane engaging portions of the holding member and the redrawing die that engage with the predrawn cup have a dynamic coefficient friction of 0.001 to 0.2, and at least one stage of drawing is effected so that a redrawing ratio defined as a ratio of the diameter of the shallowly drawn cup to the diameter of the deeply drawn cup lies within a range of 1.1 to 1.5.

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FIG. 1

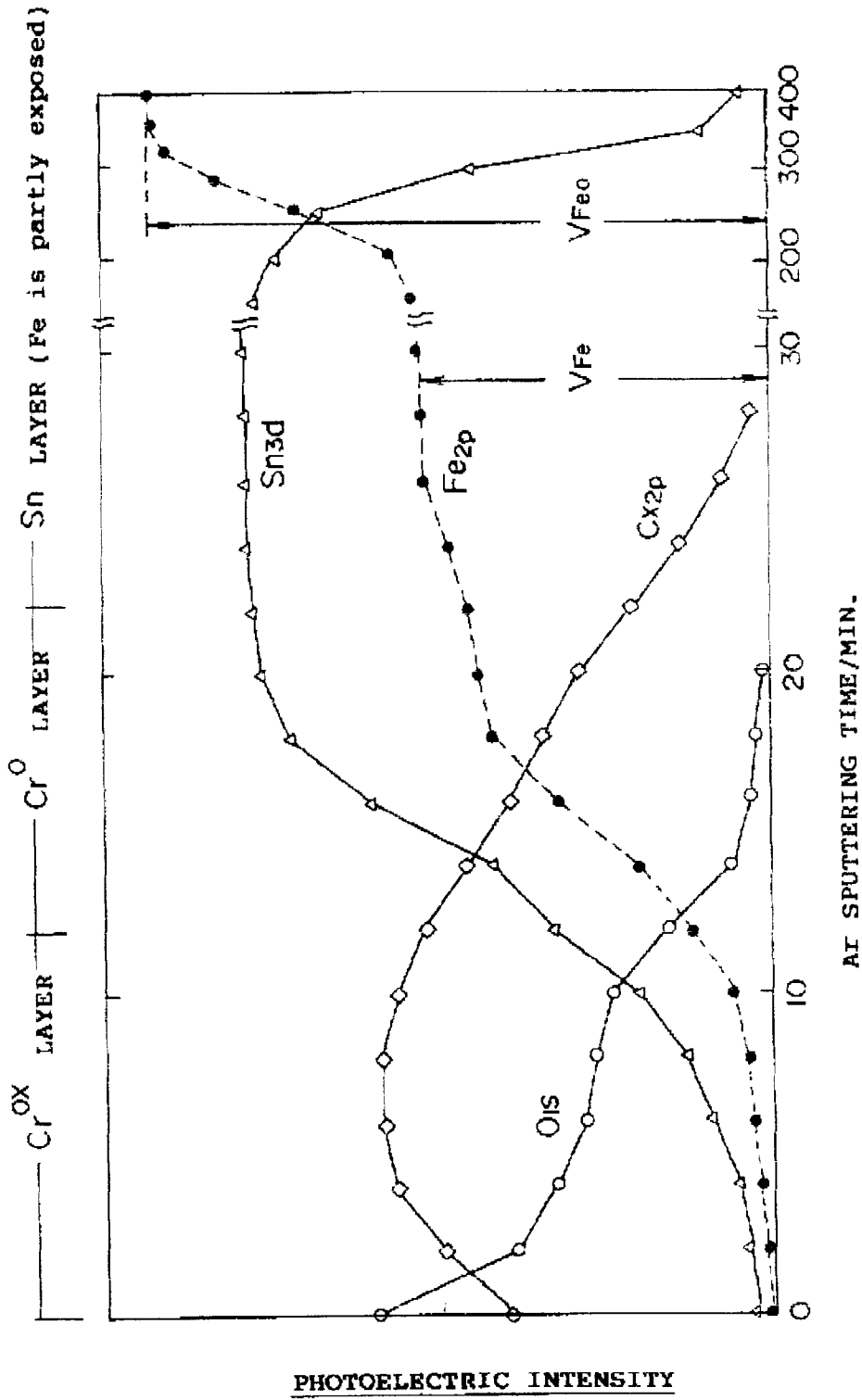


FIG. 2

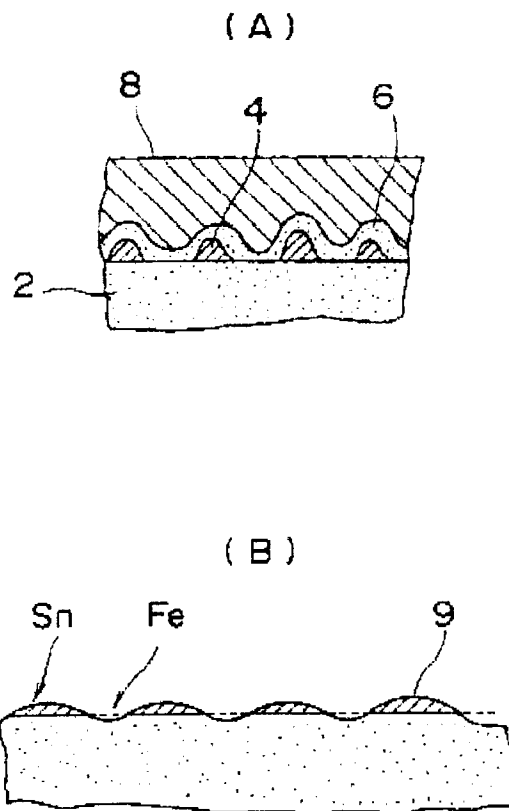


FIG. 3

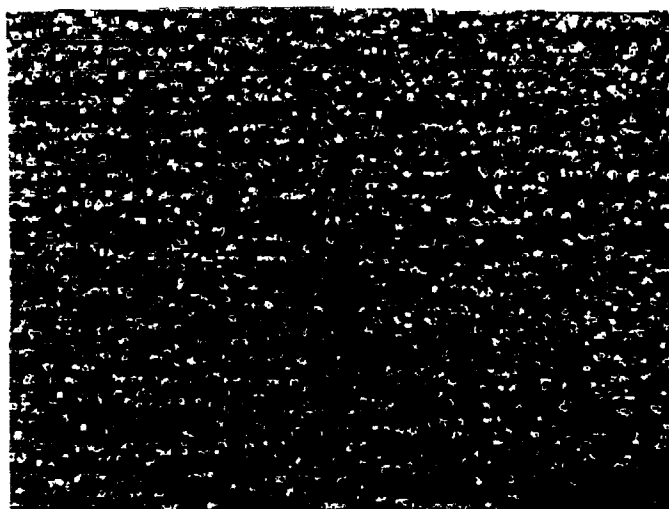


FIG. 4

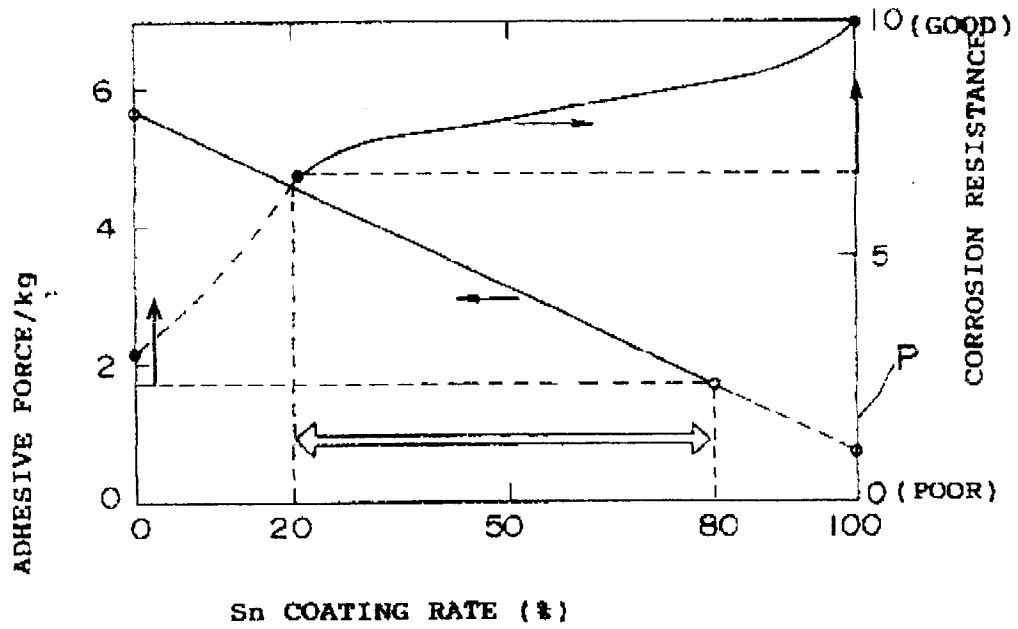


FIG. 5

